THE PYROLYSIS OF ESTERS AND RELATED COMPOUNDS

BY

W. K. RAMSAY

PART I

THE PYROLYSIS OF VINYL BENZOATE: EFFECT OF METAL CATALYSTS ON THE BREAKDOWN THRESHOLD TEMPERATURES.

PART II

THE PYROLYSIS OF BENZAL CYANIDE

by

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SUMMARY

1. Threshold temperatures in the competitive pyrolysis of vinyl benzoate.

An observation by Muir[1] suggested that one, or all, of the reactions competing in the pyrolysis of vinyl benzoate may be influenced by metallic catalysts. Further investigation now shows that the decarboxylation reaction (C^2) and the rearrangement-cum-decarbonylation (R/C^1) are catalysed by the metals present (tin, bismuth, lead, cadmium). This was suspected for the C^2 route which was thought to be partially heterogeneous; but the R/C^1 route was thought to be completely homogeneous and, therefore, independent of heterogeneous catalysis. While the test to indicate the onset of the R/C^1 route was not so satisfactory as that for the C^2 scission, the catalytic efficiency of the four metals used was identical in both reactions.

2. Pyrolysis of $PhCHX_2$: X = Br, Cl, or CN.

Both benzal bromide and benzal chloride pyrolyse at ca. 500° to produce α:α'-di-x-stilbene, thus:

$$PhCHX_2 \longrightarrow HX + {}^1/_2\ PhXC{:}CXPh$$

The bromide produces only the trans isomer, while the chloride produces both cis and trans. It was therefore probable that benzal cyanide would similarly produce α:α'-dicyanostilbene,

and from observations[20] the formation of only the trans isomer was indicated. Benzal cyanide did not, however, break down under the above conditions : and even when copyrolysed at ca. 430° with α-cyanobenzyl benzoate (a compound previously found to produce trans -α:α'-dicyano-stilbene) no substituted stilbene was found. At still higher temperatures (ca. 700°) benzal cyanide gave a complex tarry product, not characterised.

The failure of benzal cyanide to break down on the same lines as benzal bromide disproves the mechanism proposed[20] to account for the presence of α:α'-dicyano-stilbene in the pyrolysate from α-cyanobenzyl benzoate. The mechanism was thought to depend upon the formation of the intermediate $PhCH(CN)_2$, thus:

$$[\ O(CH.PhCN)_2\ ] \longrightarrow Ph.CHO + Ph.CH(CN)_2 \quad \ldots\ldots A_R'$$

$$\downarrow$$

$$HCN + {}^1/_2\ CPhCN : CPhCN$$

It is now believed that the cyanostilbene must be formed by an A° scission of α-cyanobenzyl benzoate, thus:

$$Ph.CO_2.CH.PhCN \longrightarrow Ph.CO_2H + {}^1/_2\ CPhCN : CPhCN \ \ldots\ A^\circ$$

PART I:- THE PYROLYSIS OF VINYL BENZOATE

INTRODUCTION

Threshold Temperature

In the pyrolysis of a carboxylic ester, various routes may, in general, compete with one another. The temperature at which any one specific reaction first appears during a pyrolysis is known as the threshold, or onset, temperature of that reaction. The present work is a study of the effect of metal catalysts on the threshold temperatures of routes competing in the breakdown of vinyl benzoate. It was suggested by a chance observation by Muir[1], who accidentally introduced a little Wood's metal into the reactor during a pyrolysis of cyclohexyl benzoate, and seemingly catalysed the reaction, additional breakdown routes making their appearance and a larger volume of gaseous pyrolysate being collected.

By altering variables such as flow rate and residence time, nature of reactor and packing material, contact surface area and pressure, quantitative variations can be produced in the pyrolysis of esters; while carbonised deposits in the reactor may introduce yet another variable and catalyse certain reactions[2], although more recent work by Bailey[3] and Royals[4] has refuted this conception. The apparatus used for the

present work kept all these conditions constant, thus giving a direct comparison between a catalysed and an uncatalysed vinyl benzoate pyrolysis.

During previous work in this laboratory on threshold temperatures in the pyrolysis of esters, several workers had difficulty in duplicating earlier results, though each could reproduce his own results consistently: but an apparatus later developed by Reininger[5], which was basically that used for this work, appears to have overcome this difficulty, thought to have been caused by differences in operating technique. The method is dependent upon the detection of gaseous pyrolysates in a photocell system, enabling comparisons to be made both for competitive routes in one compound and for corresponding routes in different pyrolysands (For details, see p.17).

Related Work

A synopsis of work bearing on these threshold temperatures is given below.

Norris[6], studying the pyrolytic breakdown products of hydrocarbon chains, found that the various different carbon-carbon bonds severed at different temperatures, and determined the order in which they broke. The carbon-carbon bonds in paraffin hydrocarbons are assumed to have the same heat of formation. He also observed that larger hydrocarbon chains gave lower cracking temperatures.

Extending this work to a homologous series Norris and Cresswell[7] examined the members for the cracking temperature at a particular bond. It was found that the radical present had a marked effect upon this temperature. The pyrolysis of alkyl triphenylacetates produced triphenylmethane, carbon dioxide, carbon monoxide and an alkene, probably by an A^1 scission to acid and alkene followed by secondary decarbonylation of the acid. The reaction tube, containing alkyl esters of the type $CPh_3.CO_2$ was sealed to a mercury manometer, evacuated, and heated, the following breakdown temperatures being obtained:

R	Temp.	R	Temp.	R	Temp.
CH_3	195°	C_3H_7	170°	C_4H_9	183°
C_2H_5	188°	iso-C_3H_7	155°	iso-C_4H_9	149°
				s-C_4H_9	164°

As expected from Norris' earlier work the methyl ester has the highest cracking temperature.

Petit[8] found that by suitably altering experimental conditions the order in which the bonds of an organic substance broke could be varied, this being explained by two forces; a steric factor by which stability was increased with increasing number of carbon atoms, and a polar factor which decreased stability.

Esters of high molecular weight were found by Smith and Wetzel[9] to decompose at a lower temperature than their lower homologues. As the homologous series is steadily ascended, however, the decomposition temperature alternates rather than decreases in regular steps. This is indicated in the following results obtained for cyclohexyl esters.

Formate	490°	acetate	496°	propionate	485°
butanoate	490°	pentanoate	479°	hexanoate	484°
heptanoate	473°	octanoate	478°	nonanoate	471°
decanoate	478°	octadecanoate	460°		

This temperature is known as the "characteristic temperature" being defined as the temperature at which a plot of percentage yield/pyrolysis temperature *vs.* pyrolysis temperature shows a maximum.

Smith and Bagley[10] extended the examination of ester homologues to determine whether the decreasing pyrolysis temperature was due to change in the overall molecular weight of the ester, or to change in the size of the acyl portion only. Nine isomeric esters were pyrolysed, each with molecular weight 200 and formula

$C_m H_{2m+1}.CO_2.C_nH_{2n+1}$ $(n + m = 12)$; and it was found that all the esters had a characteristic temperature within the range 558 - 62° ± 1°, showing that the

decreasing temperature was dependent upon the overall molecular weight of the ester.

Smith and Wetzel[9] also observed that the presence of electrophilic groups substituted o- and p- caused readier pyrolysis of cyclohexyl benzoate, subsequently showing that the temperature of pyrolysis was directly related to the strength of the acid from which the ester was prepared, and to the oxygen-carbon stretching bond in the infra-red spectra of the esters.

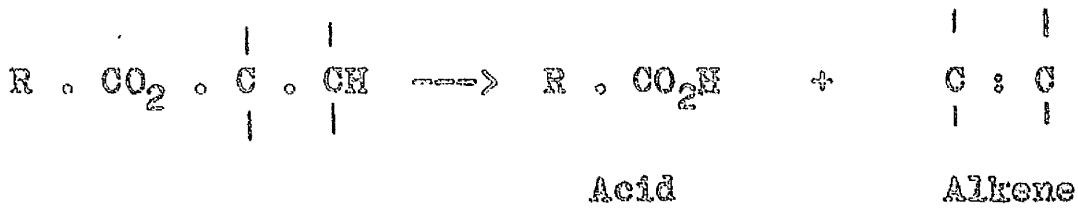
The extent of pyrolysis was found by Bailey and Hewitt[11] to be directly related to the pK_a of the corresponding acid.

The Pyrolysis of Simple Esters

Esters, as stated above, may break down by a variety of competing routes. A systematic nomenclature for these reactions was proposed by Ritchie[12].

Alkyl-Oxygen Scissions (A^1, A^o)

An A^1 scission is normally the main route by which esters with an available β-hydrogen atom on the alkyl group undergo pryolysis. An acid and an alkene are formed by scission between the alkyl group and the ether oxygen atom, followed by migration of the β-hydrogen atom to the carbonyl group. The reaction requires only moderate temperatures and occurs very smoothly.

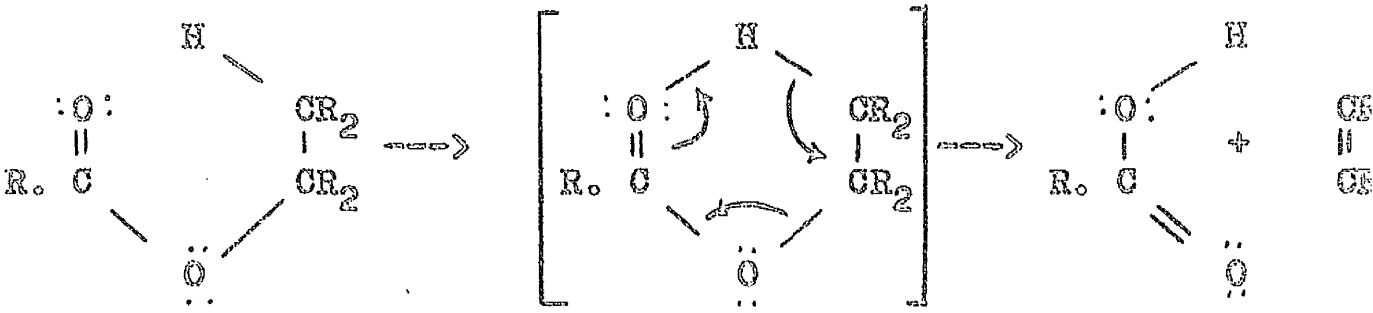


Acid Alkene

With ethyl acetate, for example, A^1 scission occurs thus :

$$Ac\ OEt \longrightarrow Ac\ OH + CH_2{:}CH_2$$

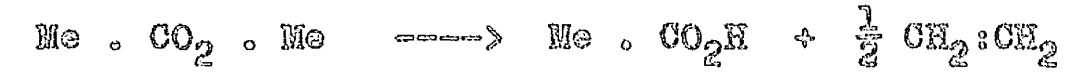
The mechanism of A^1 scission proposed by Hurd and Blunck[13] involves a transient six-membered ring with bonding of the β-hydrogen atom.



The second type of alkyl-oxygen scission (A^o scission) is undergone by alkyl esters lacking a β- but possessing an α- hydrogen atom : again acid and alkene are produced thus:

This reaction takes place at a high temperature and probably proceeds <u>via</u> a transient diradical. It is not very common.

Peytral[14] has shown methyl acetate to yield acetic acid and ethylene, as one of the reaction routes competing in its pyrolysis.



Alkenyl-Oxygen Scission (A^2)

This is another high-temperature reaction, yielding acid and alkyne in a manner similar to that of an A^1 scission. It involves the β-hydrogen atom of an unsaturated carboxylate, thus :

$$R \cdot CO_2 \cdot \overset{|}{C} : \overset{|}{CH} \longrightarrow \dot{R} \cdot CO_2H + \cdot C \vdots C \cdot$$

Acid Alkyne

Allan, Forman and Ritchie[15] have observed this as a very minor route in the complex pyrolysis of vinyl esters. For example, vinyl benzoate behaves thus (ca. 5% of the total breakdown):

$$BzO \cdot CH : CH_2 \longrightarrow BzOH + CH \vdots CH$$

Acyl-Oxygen Scissions (B^1, B^2)

Where the absence of a β-hydrogen atom prevents an A^1 breakdown, scission may occur between the acyl group and the ether oxygen atom. Migration of the hydrogen atom then follows, in either, or both, of two directions. It may travel from the acyl to the alkoxy group (B^1 scission) or from the alkoxy to the acyl group (B^2 scission).

B^1 scission yields a keten and a hydroxy compound, thus :

$$CH \cdot CO \cdot O \cdot CH \longrightarrow C : CO + HO \cdot CH$$

Keten Alcohol

The hydroxy compound may be stable (e.g. phenol) or an unstable enol (e.g. of acetaldehyde), thus :

$$Me\ CO\ .\ OPh \longrightarrow CH_2 : CO + PhOH$$

Phenyl acetate

$$Me\ CO\ .\ O\ CH : CH_2 \longrightarrow CH_2 : CO + [HO.CH:CH_2 \rightleftharpoons Me.CHO]$$

Vinyl acetate

B^2 scission, on the other hand, produces two carbonyl compounds, thus :

For example, methyl acetate and benzyl benzoate break down largely as follows :

$$Me\ CO\ .\ O\ Me \longrightarrow Me\ .\ CHO + H\ .\ CHO$$

Methyl acetate

$$BzO.\ CH_2Ph \longrightarrow 2\ Ph.\ CHO$$

Benzyl benzoate

Decarbonylation (C^1)

Direct decarbonylation of esters is uncommon, but has long been known to occur for phenyl formate :

$$H.CO\ .\ OPh \longrightarrow PhOH + CO$$

Some decarbonylations, apparently of esters, are in fact dependent upon the formation of an unstable rearrangement

product. For example, vinyl benzoate breaks down largely (ca. 75%) as follows :

$$BzO \cdot CH : CH_2 \longrightarrow [Ph.CO.CH_2.CHO] \downarrow Ph \cdot CO \cdot Me + CO$$

Decarboxylation (c^2)

This is a general reaction for esters which contain an α-unsaturated group. Phenyl acrylate and its isomer vinyl benzoate are examples, thus :

$$CH_2{:}CH.CO_2Ph \longrightarrow Ph.CH : CH_2 + CO_2$$

$$Ph.CO_2.CH{:}CH_2 \longrightarrow Ph.CH : CH_2 + CO_2$$

As can be seen unsaturation may be either olefinic or benzenoid.

No general molecular mechanism for the elimination of carbon dioxide from an α-unsaturated ester has proved acceptable, provoking the thought that the reaction may follow an ionic or free radical mechanism.

Disproportionation (D)

This is a common reaction requiring only moderate temperatures. A simple example is that of ethylidene diacetate which gives acetic anhydride and acetaldehyde on pyrolysis.

$$Ac\ O \cdot CHMe \cdot OAc \longrightarrow Ac_2O + Me \cdot CHO$$

Rearrangement (R)

This involves a simple rearrangement of the molecule to a more stable form on pyrolysis, a good example being a geometric inversion such as the following :

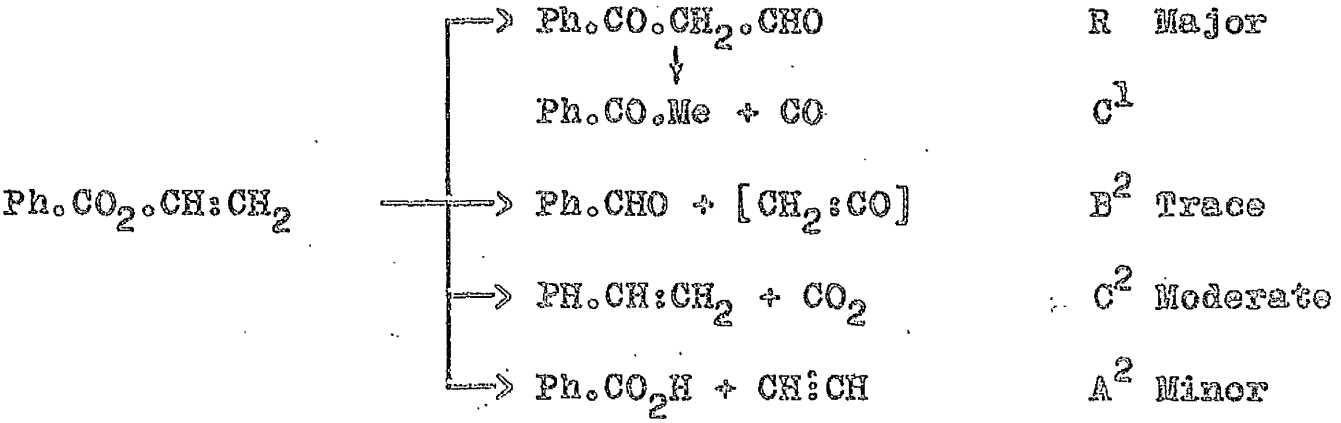
Benzyl maleate — Benzyl fumarate

Rearrangement of iso-propenyl acetate gives mainly acetylacetone (together with products of some minor competitive reactions), thus :

The Pyrolysis of Vinyl Benzoate

The pyrolysis of vinyl benzoate was studied by Allan, Forman and Ritchie[15] who found that it broke down by three routes between 350° and 500°. A fourth very minor route has more recently been observed[5].

The reaction scheme is shown below.



From an examination of the pyrolysate gas of the vinyl benzoate decomposition Steedman[16] estimated that the major route, R/C^1, accounted for 70 - 80% of the total breakdown. Of the minor routes, C^2 amounted to 10 - 20% and A^2 5 - 10% of the total breakdown. Steedman considered the pyrolysis of vinyl benzoate to be mainly homogeneous, the routes R/C^1 and A^2 being completely so, while the decarboxylation was partially heterogeneous. As has been stated before the decarboxylation reaction has never been satisfactorily explained by a molecular mechanism for α-unsaturated esters and this failure may be due to the dependance of this route upon an ionic or free radical reaction. There was no indication of participation by radical or radical chain processes in the first two routes.

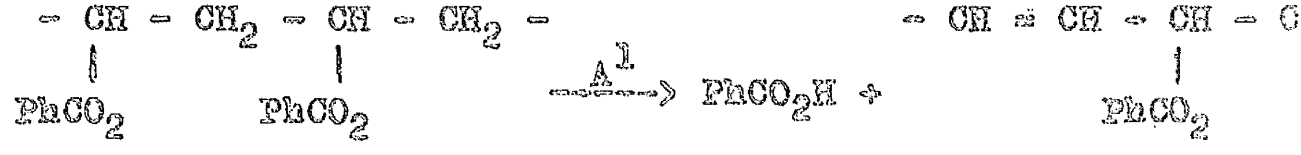
Should a free radical reaction compete in the overall scheme for the pyrolysis of vinyl benzoate, it might be possible to promote such a reaction by using a suitable catalyst. The work undertaken here was suggested by an observation by Muir[1] that a little Wood's metal produced a more vigorous evolution of gas during the pyrolysis of cyclohexyl benzoate. He assumed the Wood's metal to have catalysed one, or more, of the reactions in the pyrolysis. By using the constituents of Wood's metal (tin, bismuth, lead and cadmium) as catalysts, and studying the catalysed and uncatalysed threshold temperatures of

each reaction in the pyrolysis of vinyl benzoate, evidence of the presence of a free radical method of breakdown may be obtained for specific reactions.

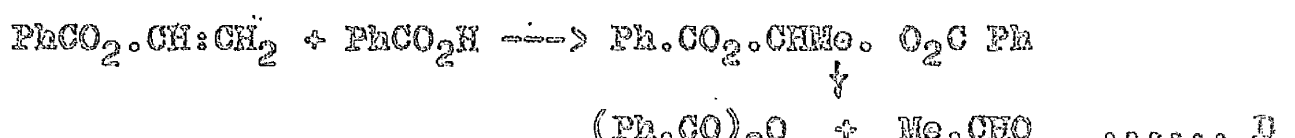
A secondary breakdown route observed by Muir[1] was the formation of methane, which resulted indirectly from the reaction between vinyl benzoate and benzoic acid to give ethylidene dibenzoate. This compound breaks down to give the acid anhydride and acetaldehyde, methane and carbon monoxide being obtained from the latter. From a study of threshold temperatures Reininger[5] was able to establish that formation of acetaldehyde and benzoic anhydride could occur at a lower temperature than the formation of benzoic acid by the A^2 route. Benzoic acid was formed at a lower temperature, the likely origin being the loss of a side chain from poly(vinyl benzoate).[17]

Stage 1 :- Partial polymerisation of vinyl benzoate.

Stage 2 :- Elimination of benzoic acid from the polyester chain (an A^1 scission).



Stage 3 :- Interaction of benzoic acid with vinyl ester following by disproportionation D.



This dual route is hereafter referred to as A^1/D.

Threshold Temperatures in Breakdown of Vinyl Benzoate

The three major primary breakdown routes in the pyrolysis of vinyl benzoate, and the secondary A^1/D route, can all be readily detected by simple chemical means. As the temperature is steadily raised, the initial formation of carbon dioxide, carbon monoxide, acetylene, and acetaldehyde in the gaseous pyrolysate indicates the threshold temperature of each of the four appropriate reactions. By testing separately for each gas, using a colorimetric detector coupled to a temperature recorder, the threshold temperature of each reaction can be determined. Any effect of catalyst, on any of these runs, should be indicated by a variation in threshold temperature. The catalysts chosen were the metals, tin, bismuth, lead, and cadmium, the constituents of Wood's metal (cf. Introduction to Part I).

Catalysis

The presence of a solid catalyst during a vapour phase reaction may produce a measurable difference in a heterogeneous reaction, but will not affect a homogeneous reaction. Steedman[16] believed that the only reaction in the pyrolysis of vinyl benzoate showing any heterogeneity was the C^2 scission, which appears to take place, in part, at the walls of the reactor, and should be the only competing reaction influenced by catalyst addition if the above argument holds.

The catalytic action of the various metals can be observed by comparing the threshold temperatures for catalysed and uncatalysed pyrolyses. A lower, or higher, threshold temperature from a particular catalysed reaction will be an indication of the catalytic effect of that metal.

There is a divergence of opinion about the mechanism of catalysis[18]. The two views held are either that the catalyst initiates the reaction at a lower temperature, or that it simply renders measurable a reaction which occurs at the lower temperature. The temperature at which pyrolyses occur suggest that the adsorption of the reactant on the catalyst is probably chemisorption, since physical adsorption normally occurs at lower temperatures and is readily reversed by heating.

Chemisorption arises from the actual formation of a chemical bond between the reactant and the catalyst surface, since the heats of adsorption are an order of magnitude higher than for physical adsorption.

Detection of the Competing Routes

Precipitate formation or colour changes are used to detect the competing routes individually in the pyrolysis of carboxylic esters.

1. The R/C^1 route is observed by the green-to-blue colour change in a 250 ml. solution of 10% phosphomolybdic acid containing 0.05 g. of polladium chloride, caused by the formation of a carbonyl complex.
2. The C^2 reaction is detected by a diluted solution of 1 ml. 1% NaOH and 0.5 ml. of 1% phenolphthalein, giving a pink to colourless change.
3. The A^2 route is detected by the precipitation of silver acetylide from a solution of 25 ml. 10% $AgNO_3$ and 70 ml. of ethanol.
4. The A^1/D route (forming acetaldehyde) is detected by the precipitation of the 2,4-dinitrophenylhydrazone.

TABLE 1

	THRESHOLD TEMPERATURES (°C)			
PYROLYSAND.	T(Me.CHO)	T (CO_2)	T(CO)	T(CH:CH)
VINYL BENZOATE	282 282	304 302 302	342 345	414 417
VINYL BENZOATE + Sn catalyst	282 284	266 268	324 327	414 416
VINYL BENZOATE + Bi catalyst	282 280	282 284	325 326 330	416 418
VINYL BENZOATE + Pb catalyst	284 282	286 290	328 330	413 416
VINYL BENZOATE + Cd catalyst	280 280	290 292	328 332	413 415

TABLE II

	THRESHOLD TEMPERATURES (°C)			
PYROLYSAND	T (Me.CHO)	T (CO_2)	T (CO)	T (CH:CH)
VINYL p-TOLUATE	294 296	302 304	346 350 352	420 422 428
VINYL p-CHLOROBENZOATE	270†	297†	330 332 335	390†
VINYL m-CHLOROBENZOATE	255†	295†	330†	386
VINYL o-CHLOROBENZOATE	235†	290†	322†	390†

† Results obtained by Reininger.[5]

RESULTS AND DISCUSSION

From the table of results (Table I) it can be seen that the presence of various catalysts in the pyrolysis of vinyl benzoate produced not only the expected difference in the threshold temperature of the C^2 reaction, but also a similar reduction in the threshold temperature of the R/C^1 reaction, which Steedman[16] believed to be a homogeneous reaction.

The A^1/D and A^2 scissions were unaffected by the addition of catalyst, although the results for the latter reaction were not reproducible with such accuracy as those for the former.

The decarboxylation of vinyl benzoate was markedly affected by the addition of catalyst. The threshold temperatures, after the addition of catalyst to the system, varied from a 10° reduction for cadmium to a 35° reduction for tin. The catalytic effect of the metals, in order of increasing efficiency, may be written:

$$Cd < Pb < Bi < Sn$$

The fact that this particular reaction is influenced by catalyst is an indication that it is heterogeneous. The vinyl benzoate is probably chemisorbed on the metal, and breaks down at a lower temperature to give styrene and carbon dioxide.

A study of the threshold temperatures of the catalysed R/C^1 route does not give such a clear picture as for the C^2 route. There is a general lowering of threshold temperature by catalyst, but the results obtained fall within a range of 8°. The apparatus is accurate only to within $\pm$ 5°, and conclusions must be viewed with caution. It is more difficult to measure the threshold temperature of the R/C^1 reaction than that of the other routes. The photocell must register a colour change which is not particularly sharp, since the green-to-blue change in the detector solution does not produce a large variation in current across the photocell.

Examination of the catalysed threshold temperatures of the R/C^1 reaction shows that the efficiency of the catalysts can be written :

$$Cd < Pb < Bi < Sn.$$

Thus the relative efficiencies of the catalysts are the same for the C^2 and R/C^1 routes. However, since the R/C^1 temperatures are very close to one another, the relative catalyst efficiency is merely suggested. The temperatures of the decarboxylation reaction can be measured very accurately, owing to the rapid colour change, with a large change in the intensity

of light passing to the photocell, and a more accurate assessment of the catalytic properties of the metals may thus be obtained. These may be reflected in the threshold temperatures of the R/C^1 reaction in presence of the corresponding catalyst.

Steedman[16] believed that the C^2 reaction of vinyl benzoate is partially heterogeneous, and the effect of catalyst upon this reaction certainly bears out this view. However, he also considered the R/C^1 route to be completely homogeneous, which does not agree with present results. Were the reaction toally homogeneous, catalyst addition would not affect it. There is a wider range of catalytic activity for the C^2 reaction; and the absence of such widely differing results for the R/C^1 route suggests that the reaction is only partially heterogeneous.

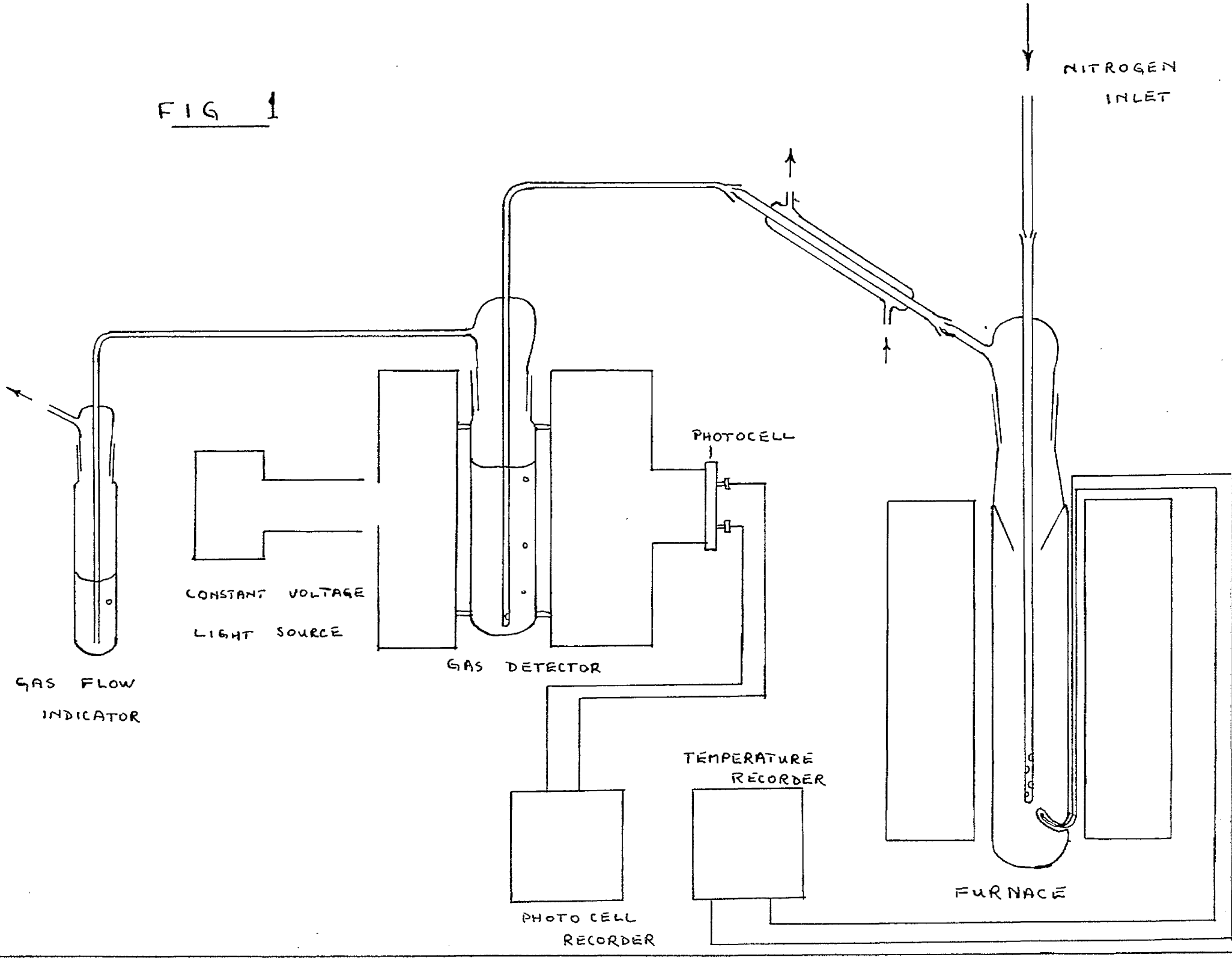
Catalytic Effect of Metals

Because of the complexity of the catalytic process it is not possible, at present, to suggest a relationship between the choice of catalyst and the threshold temperature produced. The factors governing the catalytic activity of a metal include the geometric organisation of active sites for adsorption, the rate of the adsorptive process, the thermochemistry of the adsorbate binding (taking into consideration its distribution over the

geometrical surface, competitive and co-operative adsorption, mobility of the adsorbed species, and many others. All of these points extend to the desorption of the reaction products. With such a selection of variables it is unlikely that any simple relationship can be detected among the metals tin, bismuth, lead, and cadmium, and the threshold temperatures of the C^2 route in the pyrolysis of vinyl benzoate.

These four metals were chosen solely because they compose Wood's metal, to which this problem is related. Metals more commonly associated with catalysis are those in Group VIII of the Periodic Table, in particular, iron, cobalt, nickel, platinum, and palladium. Their greater readiness to form surface complexes should result in more marked variations in the threshold temperatures.

FIG 1


NITROGEN
INLET
PHOTOCELL
CONSTANT VOLTAGE
LIGHT SOURCE
GAS DETECTOR
GAS FLOW
INDICATOR
TEMPERATURE
RECORDER
FURNACE
PHOTO CELL
RECORDER

EXPERIMENTAL

Apparatus

Vinyl benzoate was pyrolysed in a Pyrex reaction vessel, 5 inches long and 0.7 inches in diameter. Small amounts of 1/4 inch porcelain Lessing rings were added as column packing, when necessary, to prevent excessive frothing. The reaction vessel was enclosed in an electric furnace, thermostatically controlled to maintain a constant temperature to within ± 5°. The temperature was measured by a thermocouple inserted in a pocket in the reaction vessel, the terminals being connected to a Honeywell-Brown recorder, thus giving continual temperature measurement.

Threshold temperatures were measured by the method of static pyrolysis, the gases liberated in the reactions being carried over by the nitrogen stream which passed through the reactor. The pyrolysis must be carried out in an inert atmosphere to prevent the oxidation of break-down products. This was achieved by passing the nitrogen down a centre tube to near the bottom of the reaction vessel, and through the apparatus for several minutes before the beginning of a run. The gas leaving the reactor passed through a water condenser before entering a wash-bottle containing a reagent to identify the presence of a particular gas in the outlet stream.

The wash-bottle was placed in a darkened box between a constant voltage light source and a photocell. The terminals of the photocell were connected to a second Honeywell-Brown recorder and the current across the system registered on a chart. Any change in current due to reaction between the reagent in the wash-bottle and a gaseous product to give a precipitate or a colour change could immediately be seen. The gases then passed through a second wash-bottle containing water before leaving the apparatus, so that the flow rate could be maintained at a suitable steady rate (about one bubble every two seconds).

At the beginning of a run the starting points on both recorder charts were carefully marked. The recorders were differently geared and ran at different speeds, which necessitated a calculation before corresponding points on the two charts could be obtained. After the point where the change in current had occurred for a run, the time which had elapsed since the start had to be calculated from the length of paper used. The temperature corresponding to this time-interval was then found from the other recorder, showing the temperature at which any given gas X was first detected in the effluent, in other words, the threshold temperature T(X).

Procedure

The Pyrolysis of Vinyl Benzoate

1 ml. of vinyl benzoate was measured accurately into a clean reactor at the beginning of each run, the wash-bottle filled with a particular reagent, the apparatus connected, and the nitrogen flow commenced. After 15 mins. the two recorders were started simultaneously and the furnace was switched on. Attached to the furnace was a Variac resistance which enabled the rate of heating to be readily controlled. It also prevented too large a current being passed through the furnace. The temperature was initially allowed to rise at about 5° per minute. The nitrogen bubbling through the wash-bottle caused changes in intensity on the photocell, which were registered as a slight pulse on the recorder. This prevented the recorder-needle from sticking and failing to follow any intensity change in the detector liquid.

(1) The R/C[1] threshold temperature was indicated by the appearance of carbon monoxide in the reactor gases. Carbon monoxide was detected through its formation of a carbonyl complex with palladium chloride in a solution of phosphomolybdic acid. 250 ml. of a 10% solution of phosphomolybdic acid was prepared and 0.05 g. of palladium chloride added.

(2) The appearance of carbon dioxide from the C^2 route was detected by two different reagents. Initially, lime water was used, but a solution containing 1 ml. of 1% NaOH, 0.5 ml. of 1% phenolphthalein solution and 70 ml. water was later found to be more satisfactory.

(3) The A^2 threshold temperatures were obtained by detecting acetylene by means of alcoholic silver nitrate solution, silver acetylide being formed. The reagent consisted of 25 ml. of 10% $AgNO_3$ and 70 ml. of ethanol. The silver acetylide was destroyed after the run by treating it with mineral acid.

(4) The threshold temperature of the secondary A^1/D route (leading to acetaldehyde) was indicated by a solution of 2,4-dinitrophenylhydrazine, which precipitated the corresponding derivative of acetaldehyde.

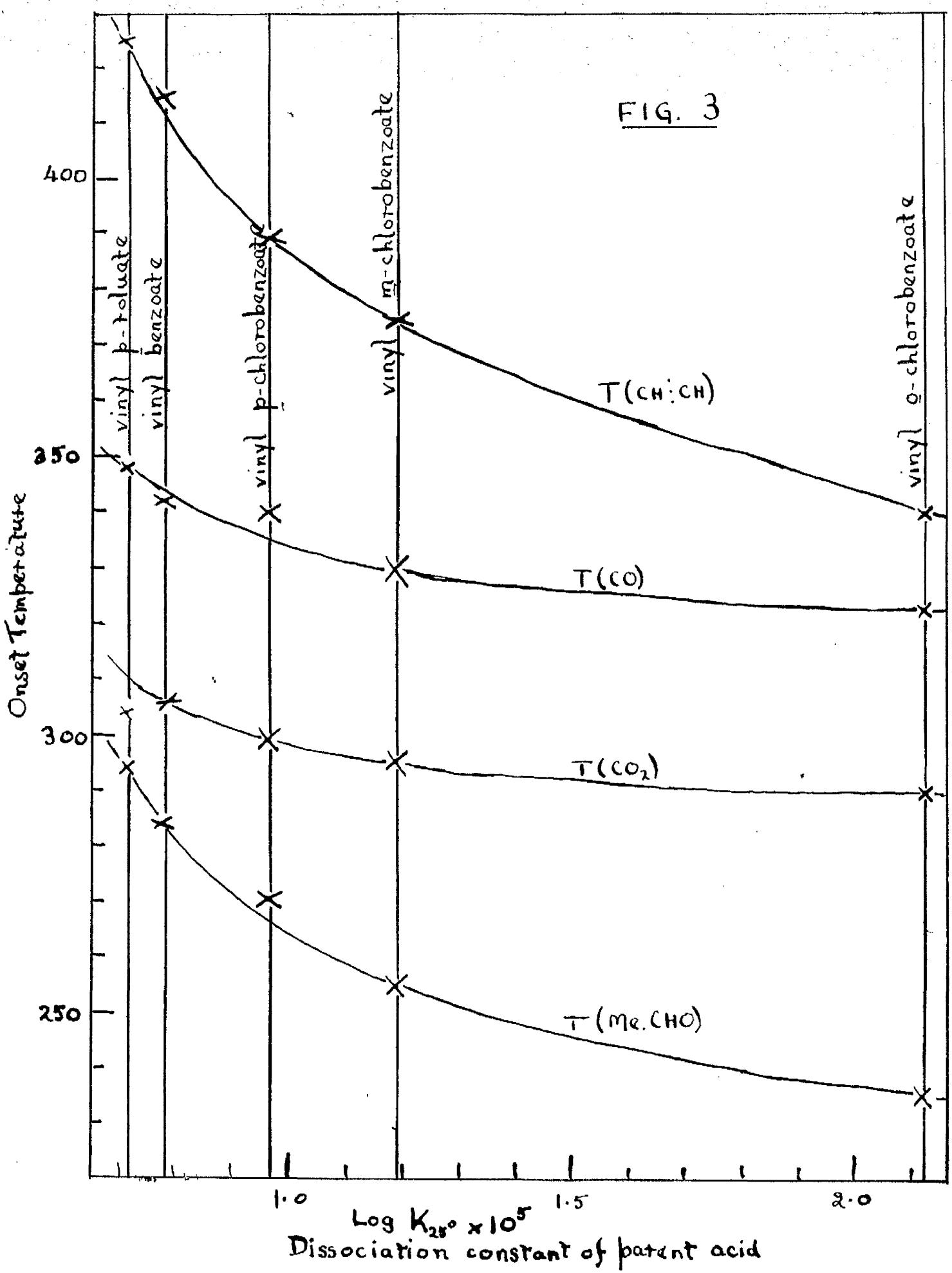
The addition of catalyst to the reactor, in the form of metal filings, induced considerable frothing, which sometimes interfered with the recording of the temperature, and it was found necessary to introduce $^1/_4$ inch porcelain Lessing rings as a packing in the reactor. In other reactions, where packing proved unnecessary, comparison between the results for a packed and an unpacked reactor showed no difference in threshold temperatures.

The method of detection of acetaldehyde and acetylene gave clear results. The recorder-chart curve showing reduction in the light reaching the photocell was easily traced to its initial starting point, and accurate threshold temperatures could thus be obtained.

Lime water was originally used to indicate the appearance of carbon dioxide, but this method proved somewhat unsatisfactory. The volume of detector solution was reduced, but the test remained rather insensitive for the C^2 reaction, although Reininger[5] found efficient precipitation. A test involving phenolphthalein was substituted and proved very sensitive. The pink solution (with NaOH) was diluted to an experimentally determined value on the recorder-chart to give the most accurate measurement of current change. When the solution turned colourless the amount of light reaching the photocell increased sharply.

The above method was an excellent example of the use of a colour change to determine the threshold temperature of a reaction. The test for carbon monoxide was, unfortunately, not so effective. A solution of phosphomolybdic acid containing palladium chloride is originally greenish-yellow, changing to bluish-green on treatment with carbon monoxide. There is, however, not much difference between the amount of

FIG. 3


400
350
300
250
Onset Temperature
vinyl p-toluate
vinyl benzoate
vinyl p-chlorobenzoate
vinyl m-chlorobenzoate
vinyl o-chlorobenzoate
T(CH:CH)
T(CO)
T(CO2)
T(Me.CHO)
1.0
1.5
2.0
Log K25° x 10^5
Dissociation constant of parent acid

light transmitted by these two solutions, and the colour change is, in any event, very gradual. It is, therefore, difficult to pin-point the exact spot on a recorder-chart where carbon monoxide was originally evolved. Unfortunately no more suitable method of testing for carbon monoxide could be devised.

Pyrolysis of Vinyl p-toluate.

A sample of vinyl p-toluate was obtained from Dr. G.W. Taylor, I.C.I., Plastics Division, Harrogate, for the determination of its theshold temperatures corresponding to the vinyl benzoate reactions.

Reininger[5] had studied the threshold temperatures of vinyl benzoate, vinyl o-, m-, and p-chlorobenzoate. By plotting the threshold temperatures of each reaction against the dissociation constant K_c of the four corresponding parent acids, he obtained curves characteristic of each of the four routes (Fig. III). The present work with vinyl p-toluate extends these curves smoothly to lower values of K_c.

The results here achieved (Table 2) were found to be in good agreement with those obtained from the graph[5] (p.26) and appears to support the idea that the threshold temperatures of this particular family of compounds can be predicted from this type of graph.

Pyrolysis of Vinyl m-chlorobenzoate

Here, no reading had been recorded by Reininger for the threshold temperature of the A^2 reaction, but a small sample (about 0.5 ml.) of his ester remained, and has now been examined without repurification in an attempt to estimate the threshold temperature. A value of 386° was obtained, quite far from the temperature predicted from the smoothed graph; but the small size and uncertain purity of the sample render this result rather unreliable.

Pyrolysis of Vinyl p-chlorobenzoate

The R/C^1 route of vinyl p-chlorobenzoate was examined to check its threshold temperature, which was found by Reininger[5] to lie just off the smoothed curve. The value now obtained, although slightly different from the original, still did not place the point on the curve. The pyrolysand was solid and some little difficulty was found in condensing unchanged pyrolysand before it reached the wash bottle.

Preparation of Vinyl Benzoate

Vinyl benzoate was prepared as described by Adelman[19]. 1 mol. of benzoic acid (120 g.) was dissolved in 4 mol. of redistilled vinyl acetate (330 g.). To the reaction mixture was added mercuric acetate (3.8 g.) and sulphuric acid (1 ml., S.G. 1.84) to produce mercuric sulphate *in situ*.

After refluxing and then cooling, anhydrous sodium acetate was added to neutralise any unreacted acid. The ester was obtained by fractional distillation (b.p. 72 - 74°/3 mm.).

By keeping the reflux temperature low and considerably increasing the time of reflux, a higher yield of greater purity is obtained. Refluxing at 35° for about 80 hrs. gives a yield of about 70%. The low temperature inhibits the formation of ethylidene diacetate, which is not readily separated from vinyl benzoate.

PART II:- THE PYROLYSIS OF BENZAL CYANIDE

INTRODUCTION

α:α'-Dicyanostilbene was found by Jones[20] as a product of the pyrolysis of α-cyanobenzyl benzoate at ca. 420°. Only the trans isomer was found in the pyrolysate. The intermediate was thought[20] to be $PhCH(CN)_2$: and the present work on this postulated intermediate was designed to confirm or refute the proposed mechanism. The related compound, benzal bromide, was pyrolysed by Jones[20], yielding trans-α:α'-dibromostilbene, after he had found both benzal bromide and trans-α:α'-dibromostilbene in the pyrolysate from α-bromobenzyl benzoate. It is believed that these two products arise from the following reaction

$$Ph.CO_2.CHPhBr \longrightarrow {}^1/2(PhCO)_2O + {}^1/2[O(CHPhBr)_2] \quad \ldots\ldots \; D$$

This unstable ether is thought to undergo an A_R^1 scission with migration of the bromine, followed by elimination of hydrogen bromide from the resulting $PhCHBr_2$ molecule

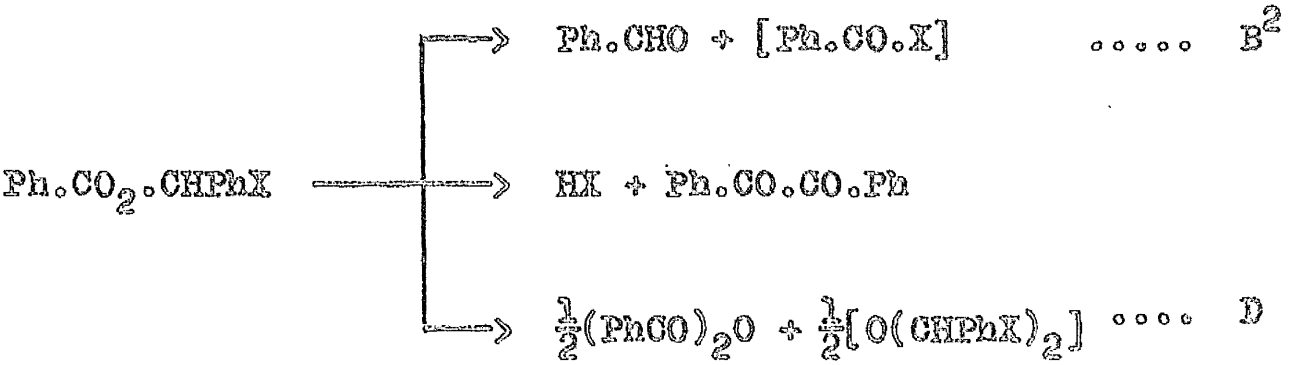
$$[O(CHPhBr)_2] \longrightarrow Ph.CHO + Ph.CHBr_2 \quad \ldots\ldots \; A_R^1$$

$$\downarrow$$

$$HBr + {}^1/_2\, CPhBr : CPhBr$$

The corresponding pyrolysis of α-cyanobenzyl benzoate produced the stilbene, but no $PhCH(CN)_2$ was found.

The generalised overall reaction scheme for the three corresponding esters to which this work is related is given below in more detail :



The three esters examined were benzyl benzoate (I; X = H), α-cyanobenzyl benzoate (II; X = CN), and α-bromobenzyl benzoate (III; X = Br).

A static pyrolysis of (I) at ca. 300° by Hurd and Bennett[21] indicated the B^2 scission to be the major breakdown route. The disproportionation product, dibenzyl ether, was not actually isolated, but its formation was inferred from the detection of benzoic anhydride and toluene. The latter is known to be formed on the pyrolysis of dibenzyl ether, along with further benzaldehyde by an A_R^1 scission. A temperature increase to ca. 500° produces[20] an unexpected minor route, yielding hydrogen and benzil. Other products of the reaction at the higher temperature are benzoic acid, benzene, benzophenone and diphenyl. A separate pyrolysis of

benzil at ca. 500° gave benzophenone and diphenyl, indicating that these two products arise from successive decarbonylations of benzil.

$$Ph.CO.CO.Ph \xrightarrow{-CO} Ph.CO.Ph \xrightarrow{-CO} Ph.Ph$$

The presence of benzene may be accounted for by partial decarbonylation of benzoic acid.

The pyrolysis of esters (II) and (III) follows, very largely, the same scheme as that of (I). Other secondary products are carbon monoxide and PhX (the known breakdown products[22,23] of Ph.CO.X) and trans-α:α'-di-X-stilbene. This is thought to arise, as mentioned previously, from an A_R^1 scission of the labile ether $[O(CHPhX)_2]$. The presence of a little benzal bromide in the pyrolysis of (III) lends support to the proposed mechanism. The trans isomers of the disubstituted stilbenes were found and a separate pyrolysis of benzal bromide by Jones[20] yielded only trans-α:α'-dibromostilbene. However, recent work has indicated[24] that benzal chloride, similarly pyrolysed, gives both cis and trans isomers of α:α'-dichlorostilbene, confirming earlier work of Leb[25].

It is hoped that a pyrolysis of benzal cyanide analogous to the bromide and chloride pyrolyses will resolve the method of formation of the disubstituted stilbene, and clarify the dissimilarity between benzal bromide and benzal chloride in forming cis- and trans-isomers of di-x-stilbene.

The relative sizes of the chlorine and bromine atoms probably account for the absence of the cis-α:α'-dibromostilbene. As both the phenyl group and the bromine atom are large the cis isomer would be sterically hindered because of the repulsion between the two bromine atoms. The chlorine atom, being smaller, will permit the formation of cis-α:α'-dichlorostilbene.

Hydrogen bromide readily converts cis-stilbene to trans-stilbene[31] and the presence of this gas in the pyrolysate from benzal bromide may favour the formation of trans-α:α'-dibromostilbene; HCl, being less readily dissociated than HBr, may not have the same effect.

TABLE III

PYROLYSAND	A	A	A	A	A	A	B	A+B
TEMPERATURE (°C)	450	550	700	600	650	700	430	430
WT. of PYROLYSAND (g.)	33	28	20	20	21	32	28	50 [10A + 40B]
FEED RATE (g/min.)	0·28	0·43	0·28	0·57	0·35	0·36	0·56	0·49
WT. of PYROLYSATE (g.)	28	22	12	15	15	15	22	41
VOLUME of GASEOUS PYROLYSATE (ml.)	250	250	1000	500	750	1000	800	1100
FREE, UNPACKED VOLUME OF REACTOR VESSEL V_c (ml.)	125	125	150	150	150	150	125	125
CONTACT TIME *t_c (secs.)	54	32	48	27	42	38	51	54

A : benzal cyanide B : α-cyanobenzyl benzoate

$$*t_c \quad \frac{3600 \times 273 \times V_c}{22,400 \times N_T \times T}$$

N_T is feed rate in mole./hr.

T is absolute temperature.

This formula was calculated by Fisher.[30]

RESULTS AND DISCUSSION

Repeated pyrolyses of benzal cyanide at temperatures ranging from 400° to as high as 700° failed to produce either *cis*- or *trans*- α:α'-dicyanostilbene. The gaseous pyrolysate was examined at all temperatures for the formation of hydrogen cyanide (which was likely to arise in any breakdown undergone by the pyrolysand) but, although temperature increase produced a corresponding rise in the amount of hydrogen cyanide evolved, no substantial quantity was liberated. It is believed that any hydrogen cyanide formed was produced following charring of the benzal cyanide in the reactor. After a pyrolysis at 700° this was particularly noticeable, a very small percentage of original material being recovered from the tars and charred matter formed. Cyanides very readily undergo complex reactions at high temperatures to form tarry residues. The runs at *ca.* 430° (the temperature at which Jones[20] produced a little dicyanostilbene) yielded very little hydrogen cyanide and left the reactor reasonably clean. Increasing the temperature by stages to the limit of the range of the glass reactor (*ca.*550°) made no significant difference in the quantity of hydrogen cyanide evolved, but recovery of the pyrolysand was made increasingly difficult by tar-formation. It

was hoped that these tarry residues might contain the expected stilbene, but investigation was fruitless. The temperature-range 600° - 700°, with a silica reactor, simply increased the amount of tar; and it thus appears that benzal cyanide, unlike benzal bromide and chloride, does not produce a disubstituted stilbene.

However, α:α'-dicyanostilbene has been found in the pyrolysate of α-cyanobenzyl benzoate[20]. It may be that one of the products of this pyrolysis catalyses the reaction to form the stilbene. If, then, a copyrolysis of α-cyanobenzyl benzoate and benzal cyanide is carried out any catalyst action will produce the stilbene from benzal cyanide. In such a pyrolysis products similar to those obtained by Jones[20] were found, but no α:α'-dicyanostilbene was isolated, the final fractions being examined for a trace of stilbene in the unchanged pyrolysand. A straight pyrolysis of α-cyanobenzyl benzoate was attempted, to no purpose; not a trace of the stilbene could be found.

These results indicate that the mechanism proposed by Jones[20] for the formation of α:α'-di-x-stilbene in the pyrolysis of α-bromobenzyl benzoate and α-cyanobenzyl benzoate does not hold for the latter breakdown. The mechanism depends on the formation of the intermediary

$Ph.CHX_2$, the bromo compound readily giving the stilbene but the cyano compound yielding none.

$$[O(CHPhX)_2] \longrightarrow Ph.CHO + Ph.CHX_2 \quad \ldots\ldots A_R^1$$

$$\downarrow$$

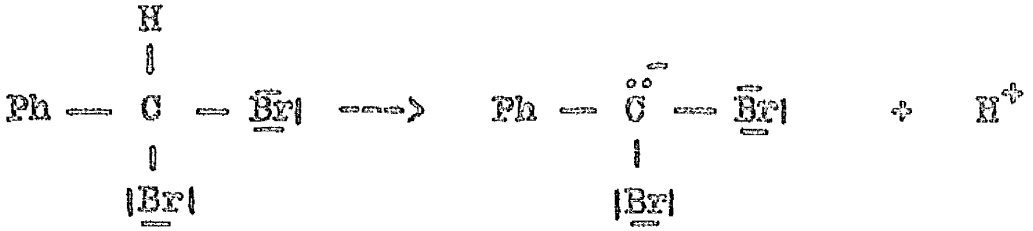
$$HX + \tfrac{1}{2}\ CPhX : CPhX$$

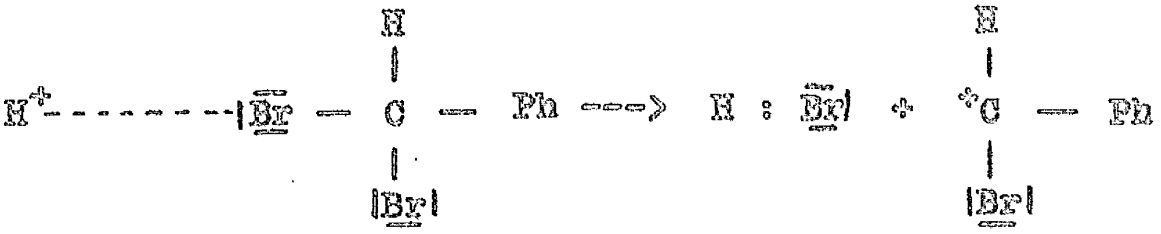
As an alternative it is suggested that the α:α'-dicyanostilbene may result from an A° scission of α-cyanobenzyl benzoate, thus :

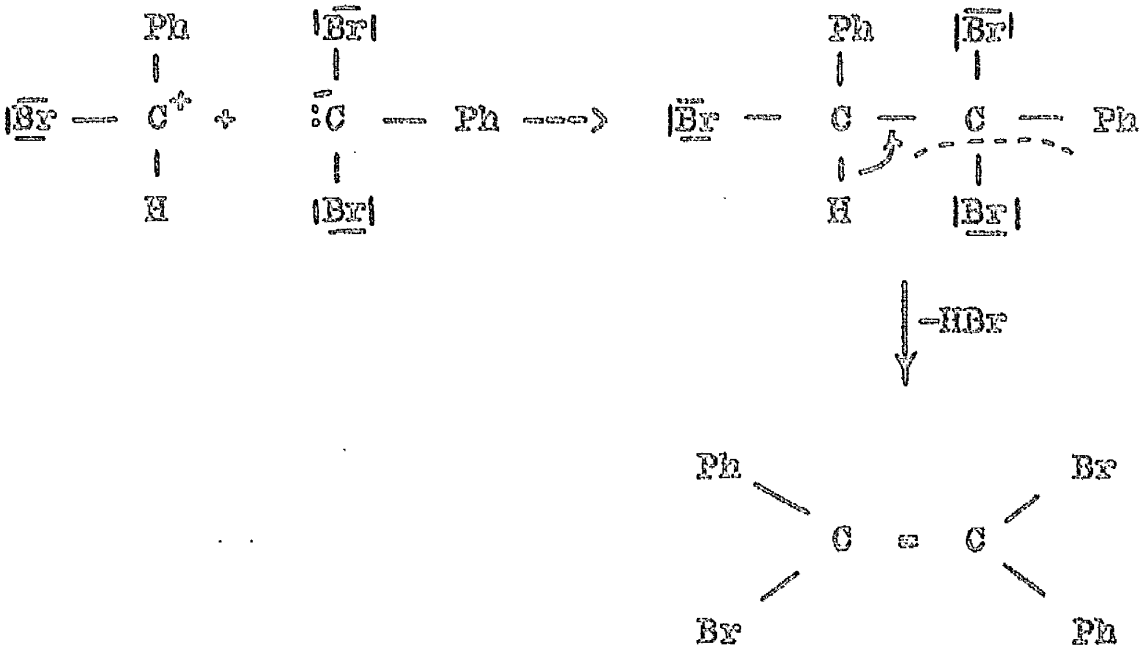
$$Ph.CO_2 . CHPhCN \longrightarrow Ph.CO_2H + \tfrac{1}{2}\ CPhCN : CPhCN \ldots\ldots A°$$

This route probably accounts for the formation of α:α'-dicyanostilbene and may also contribute to the amount of α:α'-dibromostilbene found in the pyrolysis of α-bromobenzyl benzoate.

It is apparent that in $PhCHX_2$ and $Ph.CO_2.CHPhX$ the cyanide group does not readily react in the same way as the chloride and bromide groups. A possible reaction mechanism for the formation of the disubstituted stilbene from Ph CH Br_2 is shown below.

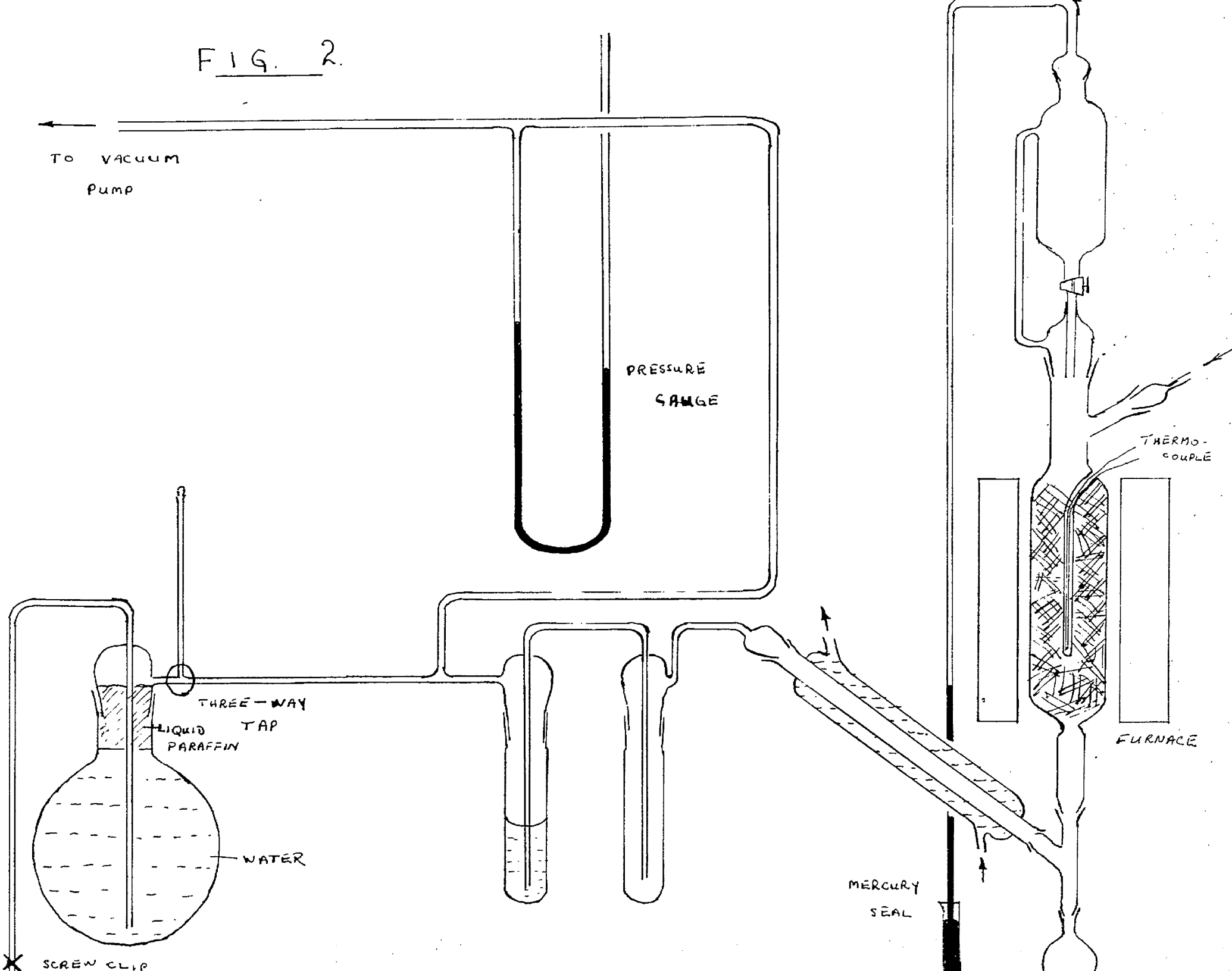






As the inductive effect (electron attraction) of the cyanide group is rather less than that of the halides there is less likelihood that the initial reaction will produce a hydrogen ion.

FIG. 2.


TO VACUUM PUMP
PRESSURE GAUGE
THERMO-COUPLE
FURNACE
THREE-WAY TAP
LIQUID PARAFFIN
WATER
MERCURY SEAL
SCREW CLIP

EXPERIMENTAL

Apparatus

The pyrolyses of benzal cyanide and α-cyanobenzyl benzoate at temperatures below 550° were carried out in a Pyrex reactor, 19 inches in length and a little greater than 1 inch in diameter, packed with short lengths of Pyrex tubing.

An electrically heated furnace, in which the pyrolysis tube hung vertically, provided a thermostatically controlled temperature to within ± 5° of the required value. The furnace temperature was measured by a thermo-couple inserted in a pocket in the reaction vessel. After being raised to the required temperature the furnace was left for 1 - 2 hours to achieve a uniform temperature and equilibrium throughout the apparatus.

Immediately before pyrolysis the system was alternately evacuated and flushed with nitrogen to remove all but minute traces of oxygen from the reactor and thus prevent oxidation of the breakdown products.

The pyrolysand was introduced to the reactor by means of a tap-funnel which allowed the material to enter the vessel at a rate of one drop every two seconds. A glass tube was fixed across the tap equalising pressure

throughout the apparatus. Another glass tube was led from the top of the tap-funnel to a mercury seal, which provided a safety valve should the pressure in the apparatus become too high. After passage through the reactor the pyrolysate was cooled in an air condenser and then collected in a 100 ml. receiver. Uncondensed gases were passed through an inclined water condenser and an alkali trap, before being collected in an aspirator. The water in the aspirator was covered with a layer of liquid paraffin to minimise solution of any water-soluble gases collected. The water exit from the aspirator was controlled by means of screw clips, constantly adjusted to maintain atmospheric pressure within the system, registered on a manometer. This also enabled the degree of evacuation of the air from the system to be noted and provided a useful check on the presence of leaks.

For temperatures greater than 550° a silica reactor was substituted for the Pyrex vessel. This tube was 12 inches long and 1.5 inches in diameter, packed throughout with small pieces of silica tube. Another similar furnace had to be used with this reactor, since its dimensions differed considerably from the first.

As the pyrolysands were solid they were melted in the reservoir, by means of a heating tape, before admission to the reactor.

PROCEDURE

The pyrolysis of benzal cyanide

1. At 450°

Pyrolysis of benzal cyanide at this temperature produced only a very small volume of gas (250 ml.). Much of this volume must have been due to the method of collecting the gaseous pyrolysate, the water-flow from the aspirator being manually controlled to offset the pressure rise in the apparatus. Vaporisation of the pyrolysand on entering the reactor produced a pressure increase, nullified by subsequent condensation. The volume of gas collected, being so small, is not significant.

The pyrolysate was distilled at reduced pressure (b.p. 150 - 170°/5 mm.) but no trace of α:α'-dicyano-stilbene was observed. The distillation recovered a great deal of pyrolysand but left a considerable tarry residue in the flask. The reactor, after pyrolysis, was covered with light brown charring.

2. At 550°

Pyrolysis at this temperature produced results comparable with those at the lower temperature, although charring in the reactor was much more noticeable and less pyrolysand was recovered from the pyrolysate. Again only 250 ml. of gas were collected.

3. At 600°

At this temperature it was necessary to use the silica reactor. There was considerable charring, both in the pyrolysate and in the reactor, and a much smaller percentage of the pyrolysand was recovered. The gas collected in this run was 500 ml. A 10% NaOH solution was used to trap any hydrogen cyanide evolved and the solution in the trap titrated against standard 0.1 $\bar{N}$ $AgNO_3$

$$1 \text{ ml. } 0.1 \bar{N} AgNO_3 \equiv 0.0054 \text{ g. } HCN$$

The hydrogen cyanide evolved in this run was 0.087 g., which was 2.3% of theoreitcal yield for the formation of $\alpha:\alpha^1$-dicyanostilbene.

4. At 650°

The volume of gaseous pyrolysate was about 750 ml. The charring was far more apparent, and 5.3% of hydrogen cyanide was obtained.

5. At 700°

The pyrolysate produced yielded very little material on distillation. The reactor was practically choked by the amount of charred material left in it, particularly at the entrance, and the receiver contained mainly high-boiling tars. The amount of hydrogen cyanide liberated was 8.8%.

It must be assumed that in the above reactions the hydrogen cyanide formed must come from the complex reactions producing the high-boiling viscous tars left in the receivers after pyrolysis. These tars were treated with a variety of solvents after fractionation in an effort to detect traces of the stilbene. In many cases small samples of a powder were obtained, with a wide melting point range. Two consecutive extractions of a residue did not guarantee products approximating to each other in melting point.

The pyrolysis of α-cyanobenzyl benzoate

The pyrolysate from a run at 430° yielded the following fractions.

Fraction	Temperature	Weight
1	110 - 120°/30 mm.	1 g.
2	120 - 150° "	1 g.
3	150 - 170° "	2 g.
4	170 - 200° "	2 g.
5	200 - 230° "	1 g.
6	230 - 250° "	0.5 g.
7	150 - 180°/5 mm.	1 g.
8	180 - 200° "	3 g.
9	200 - 210° "	0.5 g.

Fractions 1 - 3 contained benzoic acid (m.p. and mixed m.p. 120 - 121° : lit 121°), benzaldehyde (2,4-dinitrophenylhydrazone m.p. 167° : lit 169°), and benzonitrile (converted to benzamide[26] m.p. 124 - 5° : lit 125 - 6°, 130°). Fractions 4 - 6 (solid) consisted solely of benzoic acid. Fractions 7 - 9 were obtained after reducing the pressure to 5 mm. Fraction 7 consisted of benzoic acid, while fractions 8 and 9 were unchanged pyrolysand. The last two fractions were carefully examined for the presence of α:α'-dicyanostilbene. Crystals appearing in the last fraction were filtered and found to be unchanged pyrolysand, m.p. 58°. Both fractions solidified quite quickly.

The copyrolysis of benzal cyanide and α-cyanobenzyl benzoate.

A mixture of 40 g. of α-cyanobenzyl benzoate and 10 g. of benzal cyanide was pyrolysed at 430° and the breakdown products fractionated at 3 mm. pressure.

Fraction	Temperature	Weight
1	75 - 100°	2 g.
2	100 - 120°	4 g.
3	120 - 150°	2 g.
4	150 - 180°	5 g.
5	180°	4 g.
6	180 - 184°	6 g.
7	184 - 208°	3 g.
Residue		12 g.

Fractions 2 - 7 solidified very quickly thus preventing recognition of the stilbene as a solid suspended in a liquid fraction. Fraction 1 (liquid) contained benzaldehyde, benzonitrile, and benzoic acid, while in fraction 2 these three compounds appeared again but with benzoic acid predominating. Fraction 3 consisted of benzoic acid and benzal cyanide; fraction 4 contained only the latter. Fractions 5, 6 and 7 contained α-cyano-benzyl benzoate.

Determination of hydrogen cyanide.

60 ml. of 10% NaOH was placed in a trap before the pyrolysis. After the reaction 10 ml. of the alkali trap solution was diluted with 100 ml. of distilled water. 0.1$\bar{N}$ $AgNO_3$ solution was titrated against this solution, a sharp end-point being obtained by adding 5 ml. of 5$\bar{N}$ ammonia solution and a few drops of 0.1$\bar{N}$ potassium iodide solution.

1 ml. 0.1$\bar{N}$ $AgNO_3$ = 0.0054 g. HCN

Thus the weight of hydrogen cyanide absorbed by the total alkali in the trap can be estimated.

The preparation of α-cyanobenzyl benzoate.

This compound was prepared by the method of Francis and Davis[27] from 53 g. of benzaldehyde and 70 g. of benzoyl chloride shaken up with an aqueous solution of 33.5 g. (2% excess) of potassium cyanide. The flask was cooled; solid α-cyanobenzyl benzoate separated out overnight. A yield of 70 g. (59%) was obtained, recrystallised from ethanol, m.p. 59° (lit. m.p. 60°)

$Ph.CHO + Ph.CO.Cl + KCN \longrightarrow Ph.CO_2.CHPh.CN + KCl$

The preparation of benzal cyanide.

This was prepared from benzyl cyanide as described by Hessler[28].

Preparation of ethyl phenylcyanoacetate.

112 g. of benzyl cyanide was gradually added to a solution of 112 g. of ethyl carbonate and 700 ml. of anhydrous ether containing 22 g. of sodium in small pieces. After 20 mins. the solution became pale yellow and bubbles of gas (hydrogen) were evolved. The temperature increased with the rate of the reaction, necessitating the use of "Drikold" to prevent the ether from boiling. After 2 hours the reaction ceased and the dark red liquid was left overnight, during which time large quantities of solid separated. The mechanism is :

$$Ph.CH_2.CN \xrightarrow{Na} Ph.CHNa.CN + \tfrac{1}{2} H_2$$

$$\downarrow$$

$$Ph.CH(CN).CO_2Et + EtONa$$

The ester was separated by acidifying the solution with dilute sulphuric acid, evaporating off the ether, and fractionating the product at reduced pressure. The fraction distilling at 150 - 180°/15 mm. was redistilled, collected, and weighed. The pure ester is a colourless oil, b.p. 165.5°/20 mm., the yield being 55 g. (30.2% theoretical based on benzyl cyanide).

Preparation of α:α-cyanophenylacetamide.

55 g. of ethyl phenylcyanoacetate were treated with 64 g. of conc. aqueous NH_3, and the amide separated from the solution overnight.

$$Ph.CH(CN).CO_2Et \xrightarrow[conc.aq.]{NH_3} Ph.CH(CN).CONH_2$$

The yield was 30 g. (64%), reprecipitated from ethanol m.p. 146° (lit.147°).

Preparation of benzal cyanide.

It was found that the use of large quantities of α:α-cyanophenylacetamide and phosphorus penta chloride, to produce benzal cyanide, nearly doubled the percentage yield, this stage of the reaction having normally given a low yield.

60 g. of α:α'-cyanophenylacetamide and 32 g. of phosphorus pentachloride were placed in a distillation flask evacuated to 5 mm. ; the flask was maintained at a low temperature while the solid melted and reacted, water being removed from the amide. The light coloured liquid became darker and much more viscous as the reaction progressed. The temperature was then raised and the

benzal cyanide came over, solidifying in the condenser.

$$Ph.CH(CN).CO.NH_2 \xrightarrow{-H_2O} Ph.CH(CN)_2$$

The yield was 20 g. (40%); the benzal cyanide was recrystallised from ether and light petroleum giving plates, m.p. 67 - 69° (lit. m.p. 67 - 69° [28], 70 - 71° [29]).

REFERENCES

1. Muir, Ph.D. Thesis, Glasgow University, 1959.
2. Houtmann, van Steenis, and Heertjes, Rec.Trav.Chim., 1946, 66, 781.
3. Bailey and Hale, J.Amer.Chem.Soc., 1959, 81, 643.
4. Royals, J.Org.Chem., 1958, 23, 1822.
5. Reinhager, Ph.D. Thesis, Glasgow University, 1961.
6. Norris, J.Chem.Ed., 1932, 9, 1890.
7. Norris and Cresswell, J.Amer.Chem.Soc., 1934, 56, 423.
8. Petit, Bull.soc.chim., 1943, 10, 224.
9. Smith and Wetzel, J.Amer.Chem.Soc., 1958, 80, 875.
10. Smith and Bagley, J.Org.Chem., 1959, 24, 128.
11. Bailey and Hewitt, J.Amer.Chem.Soc., 1956, 21, 543.
12. Ritchie, Chem. and Ind., 1954, 37.
13. Hurd and Blunck, J.Amer.Chem.Soc., 1938, 60, 2419.
14. Peytral, Bull.soc.chim., 1922, 31, 113.
15. Allan, Forman, and Ritchie, J., 1955, 2717.
16. Steedman, Ph.D. Thesis, Glasgow University, 1959.
17. Grassie, J.Polym.Sci., 1959, 39, 211.
18. Parlin, Wallenstein, Zwolinski, and Eyring, "Catalysis", Reinhold Publishing Corp., 1955, Vol.II, 255.
19. Adelman, J.Org.Chem., 1949, 14, 1057.

20. Jones and Ritchie, J., 1958, 4515.

21. Hurd and Bennett, J.Amer.Chem.Soc., 1929, 51, 1197.

22. Bennett, Jones and Ritchie, J., 1956, 2628.

23. Ladacki, Leigh, and Szwarc, Proc.Roy.Soc., 1952, A, 214, 273.

24. Ramsay, B.Sc. Thesis, Glasgow University, 1960.

25. Lob, Ber., 1903, 36, 3069.

26. Radziszewski, Ber., 1885, 18, 355.

27. Francis and Davis, J., 1909, 95, 1403.

28. Hessler, Amer.Chem.J., 1904, 32, 123.

29. Flurscheim and Holmes, J., 1928, 2237.

30. Fisher, Ind.Eng.Chem., 1942, 34, 473.

31. Finer, "Organic Chemistry", Longman's, Green, 1959, Vol.II, p.121.